809. *Molecular Polarisability: Molar Kerr Constants, Apparent Dipole Moments, and Conformations of Trialkyl Borates as Solutes.*

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Twelve trialkyl borates as solutes in carbon tetrachloride show properties consistent with conformations in which the BO_3 unit is a triangular plane with the O–C bonds so rotated that each is at *ca.* 74° to a direction normal to this plane. During step-wise ascent of the series $B(OC_nH_{2n+1})_3$ each added C–C link appears to make semi-tetrahedral angles with the principal polarisability directions of the molecule being increased.

A review [1] of the physical properties of trialkyl borates, $B(OR)_3$, included the facts that Raman and infrared spectra indicate C_{3h} symmetry, and that electron diffraction measurements show the BO_3 nucleus to be planar, as it appears, from Cowley's *X*-ray study,[2]

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[1] Lappert, *Chem. Rev.*, 1956, **56**, 959.

[2] Cowley, *Acta Cryst.*, 1953, **6**, 522.

to be in boric acid. At least seven borates[3] have dipole moments of *ca.* 0·8 D. Smyth[4] notes that such polarity arises from the distribution of the R–O vectors about the B–O bond directions, although[3c] it is too small to be explained by " free rotations " of the bent B–O–R units, steric repulsions among the alkyl groups evidently reducing the stabilities of the high-moment configurations (ref. 4, p. 373). The implication here is that each borate is a mixture of individual conformational isomers manifesting normal orientation polarisations. However, in the light of Coop and Sutton's work,[5] a moment of 0·8 D could also be ascribed to vibration polarisation, owing to the restricted movements (librations) of the alkyl groups within limits above and below the BO_3 plane.

It is difficult to decide between these alternatives. Present measurements were begun to ascertain the algebraic signs of the molar Kerr constants of a number of borates because of the chance that these might be negative, in which eventuality (for reasons given in ref. 6, p. 294) the existence of permanent resultant moments would be established. Unfortunately, in the outcome, all ${}_{\infty}({}_{\mathrm{m}}K_2)$'s have proved positive; nevertheless their magnitudes provide some useful evidence not hitherto available.

EXPERIMENTAL

Nine alkyl borates have been studied in carbon tetrachloride as solvent, previously described procedures for the measurement of dielectric constant, electric birefringence, etc., being followed.[6,7] Methyl borate was prepared by the method of Schlesinger *et al.*,[8] the others were commercial specimens redistilled immediately before the solutions were made up. Symbols, methods of calculation, and headings used in the following Tables are explained in ref. 6, pp. 280—283. The various constants adopted for carbon tetrachloride at 25° are:

$$\begin{array}{lll} \varepsilon_1 = 2{\cdot}2270 & (n_{\mathrm{D}})_1 = 1{\cdot}4575 & H = 2{\cdot}060 \\ d_1 = 1{\cdot}58454 & p_1 = 0{\cdot}18319 \text{ c.c.} & J = 0{\cdot}4731 \\ B_1 = 0{\cdot}070 \times 10^{-7} & C = 0{\cdot}10596 & {}_sK_1 = 0{\cdot}749 \times 10^{-14} \end{array}$$

In no case was a change in the Kerr constant of the solvent detected on dissolution of the borate up to weight fractions of 20%; the coefficient δ is therefore zero throughout.

The results are tabulated.

DISCUSSION

The dipole moments and refractivity data of Table 2 are in general accord with previous determinations, where these exist.[1,3,9] Table 3 shows that trialkyl borate molecules are only slightly anisotropically polarisable. Estimates of the unknown longitudinal polarisability, $b_{\mathrm{L}}^{\mathrm{BO}}$, of the B–O bond are $0{\cdot}055 \times 10^{-23}$ (by Le Fèvre's 1958 equation[10]) or $0{\cdot}053 \times 10^{-23}$ (by the 1959 equation[10]); for both, the B–O intercentre distance[11] of 1·38 Å is used. Becher[11] recognises a B–O valency vibration in the infrared spectrum at 1360 cm.$^{-1}$ and another in the Raman spectrum at 727 cm.$^{-1}$, the latter line being polarised. With $\nu = 1360$ cm.$^{-1}$, $b_{\mathrm{L}}^{\mathrm{BO}}$ emerges as $0{\cdot}23_5 \times 10^{-23}$, which is impossibly great since $b_{\mathrm{L}}^{\mathrm{BO}} + b_{\mathrm{T}}^{\mathrm{BO}} + b_{\mathrm{V}}^{\mathrm{BO}}$ is only $0{\cdot}196_6 \times 10^{-23}$ if R_{D} for the B–O link is 1·74 c.c. as stated by Gillis.[9] Accordingly, assuming that $b_{\mathrm{T}}^{\mathrm{BO}} = b_{\mathrm{V}}^{\mathrm{BO}}$, we have:

$$10^{23}b_{\mathrm{L}}^{\mathrm{BO}} = 0{\cdot}053,\ 10^{23}b_{\mathrm{T}}^{\mathrm{BO}} = 10^{23}b_{\mathrm{V}}^{\mathrm{BO}} = 0{\cdot}072$$

These values, in conjunction with $10^{23}b_{\mathrm{L}}^{\mathrm{C-O}} = 0{\cdot}081$, $10^{23}(b_{\mathrm{T}}^{\mathrm{C-O}} = b_{\mathrm{V}}^{\mathrm{C-O}}) = 0{\cdot}039$, and

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[3] (*a*) Cowley and Partington, *Nature*, 1935, **136**, 643; (*b*) Otto, *J. Amer. Chem. Soc.*, 1935, **57**, 1476; (*c*) Lewis and Smyth, *J. Amer. Chem. Soc.*, 1940, **62**, 1529.

[4] Smyth, " Dielectric Behaviour and Structure," McGraw-Hill, New York, 1955, p. 379.

[5] Coop and Sutton, *J.*, **1938**, 1269.

[6] Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.*, 1955, **5**, 261.

[7] Le Fèvre and Le Fèvre, *J.*, 1953, 4041; 1954, 1577.

[8] Schlesinger, Brown, Mayfield, and Gilbreath, *J. Amer. Chem. Soc.*, 1953, **75**, 213.

[9] Gillis, " Bond Refractions of Single Covalencies," Tech. Note 51, Defence Standards Laboratories, Maribyrnong, Vic., Australia; *Rev. Pure Appl. Chem.*, 1960, **10**, 21.

[10] Le Fèvre, *Proc. Chem. Soc.*, 1958, 283; 1959, 363.

[11] Becher, *Z. phys. Chem. (Frankfurt)*, 1954, **2**, 276.

TABLE 1. *Densities, dielectric constants, and refractions, for solutions of borates in carbon tetrachloride at 25°.*

Trimethyl borate

10^6w_2	d_{12}	ε_{12}	n_{12}
12,959	1·56975	2·2384	1·4557
17,643	1·56526	2·2380	1·4542
29,697	1·55265	2·2407	1·4522
42,407	1·53855	2·2487	1·4501
53,122	1·52573	2·2543	1·4480
64,780	1·51486	2·2612	1·4460
74,635	1·50197	2·2664	1·4443
89,931	1·48733	2·2721	1·4420

Tri-isopropyl borate

10^6w_2	d_{12}	ε_{12}	n_{12}
15,351	1·56473	2·2306	1·4558
27,728	1·54826	2·2346	1·4543
35,135	1·53817	2·2359	1·4535
43,474	1·52734	2·2366	1·4525
53,846	1·51342	2·2381	1·4514
66,559	1·51342	2·2404	1·4501
79,731	1·47938	2·2446	1·4486
90,483	1·46322	2·2453	1·4474

Tri-isobutyl borate

10^6w_2	d_{12}	ε_{12}	n_{12}
11,986	1·56862	2·2286	1·4564
21,689	1·55603	2·2293	1·4555
34,294	1·53937	2·2313	1·4544
49,266	1·51972	2·2347	1·4529
61,136	1·50385	2·2368	1·4519
76,473	1·48301	2·2379	1·4505
97,348	1·45519	2·2412	1·4486
118,273	1·42822	2·2457	1·4482

Tripentyl borate

10^6w_2	d_{12}	ε_{12}	n_{12}
22,423	1·55276	2·2302	1·4562
32,687	1·53782	2·2311	1·4555
42,803	1·52386	2·2330	1·4547
56,031	1·50471	2·2341	1·4539
69,124	1·48613	2·2373	1·4532
82,209	1·46791	2·2369	1·4524
95,760	1·44833	2·2369	1·4515

Trihexyl borate

10^6w_2	d_{12}	ε_{12}	n_{12}
18,642	1·55903	2·2280	1·4565
28,731	1·54577	2·2305	1·4560
41,256	1·52810	2·2313	1·4554
55,773	1·50926	2·2332	1·4545
66,821	1·49233	2·2362	1·4540
81,038	1·47413	2·2362	1·4532

Trioctyl borate

10^6w_2	d_{12}	ε_{12}	n_{12}
14,529	1·56362	2·2278	1·4567
23,188	1·55123	2·2286	1·4564
38,410	1·52937	2·2306	1·4556
53,862	1·50766	2·2313	1·4549
77,107	1·47208	2·2342	1·4538
86,051	1·46088	2·2345	1·4534
100,468	1·44102	2·2364	1·4526

Trinonyl borate

10^6w_2	d_{12}	ε_{12}	n_{12}
10,123	1·56983	2·2282	1·4570
28,658	1·54367	2·2288	1·4554
41,310	1·52536	2·2290	1·4560
52,341	1·50937	2·2303	1·4555
70,036	1·48418	2·2310	1·4549
83,710	1·46441	2·2316	1·4544
98,125	1·44385	2·2316	1·4539
109,234	1·42590	2·2331	1·4535

10^6w_2	n_{12}	10^6w_2	n_{12}
Tri-n-propyl borate		*Tri-n-butyl borate*	
14,042	1·4559	15,632	1·4556
28,002	1·4542	28,735	1·4545
36,468	1·4532	41,156	1·4535
61,178	1·4502	54,022	1·4521

TABLE 2. *Polarisations at infinite dilution, molecular refractions, and apparent dipole moments.**

Borate	$\alpha\varepsilon_1$	$-\beta$	$-\gamma$	$_\infty P_2$ (c.c.)	R_D (c.c.)	μ (D)
Trimethyl	0·52	0·689	0·120	$37·8_8$	$24·1_1$	$0·8_2$
Triethyl	(0·38)	(0·706)	(0·092)	$50·3_0$	$36·6_3$	$0·7_5$
Tri-n-propyl	(0·23)	(0·837)	0·080	$65·0_0$	$52·7_3$	$0·7_7$
Tri-isopropyl	0·22	0·834	0·067	$67·5_7$	$52·4_6$	$0·8_6$
Tri-n-butyl	(0·16)	(0·843)	0·069	$78·7_7$	$66·3_3$	$0·7_7$
Tri-isobutyl	0·15	0·834	0·060	$80·9_8$	$65·9_8$	$0·7_7$
Tri-s-butyl	(0·15)	(0·843)	(0·058)	$78·8_1$	$66·4_4$	$0·8_5$
Tripentyl	0·13	0·897	0·044	$94·7_4$	$80·3_3$	$0·8_4$
Tri-isopentyl	(0·12)	(0·894)	(0·045)	$94·3_5$	$80·2_0$	$0·8_1$
Trihexyl	0·10	0·861	0·040	110·5	$95·2_5$	$0·8_6$
Trioctyl	0·09	0·907	0·032	139·4	121·2	$0·9_7$
Trinonyl	0·06	0·905	0·025	$156·5_5$	139·0	$0·9_3$

* Data in parentheses were calculated from ε, d, and n_D measurements given in ref. 3.

$b_L^{CH} = b_T^{CH} = b_V^{CH} = 0·064 \times 10^{-23}$ c.c. (see refs. 6 and 12), may now be applied to trimethyl borate.

For this ester we have $R_D = 24·11$ (Table 2), whence an estimate of $b_1 + 2b_3$ is $2·72_4 \times 10^{-23}$ c.c. For the flat arrangement of $B(OMe)_3$, b_1 is the sum of the "vertical"

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[12] Le Fèvre and Le Fèvre, *J.*, 1956, 3549.

polarisabilities of the bonds involved, *i.e.*, $b_1 = 0{\cdot}909 \times 10^{-23}$ c.c., so that $b_2 = b_3 = 0{\cdot}907 \times 10^{-23}$ c.c. These differ somewhat from either of the sets shown in Table 3. If each of the C–O bonds is inclined at an angle θ to a line perpendicular to the OOO triangle and passing through the boron atom, we have: $0{\cdot}919 = 3b_{\mathrm{V}}^{\mathrm{BO}} + 9b_{\mathrm{V}}^{\mathrm{CH}} + 3(b_{\mathrm{L}}^{\mathrm{C-O}} \cos^2\theta + b_{\mathrm{T}}^{\mathrm{C-O}} \sin^2\theta)$, whence θ is *ca.* 74°, *i.e.*, the three O–C bonds are disposed towards the defined line much as they would be towards a fourth bond if attached to a quadrivalent tetrahedral atom. The apparent moment may therefore be largely real, for if $\mu_{\text{Me-O}}$ is between 0·74 (ref. 4, p. 244) and 1·1 D (from [13] $\mu_{\text{Me}_2\text{O}} = 1{\cdot}25$ D and the Me–O–Me angle = 110°), $\mu_{\text{B(OMe)}_3}$ should be between 0·61 and 0·91 D, to be compared with $\mu_{\text{expt.}} = 0{\cdot}82$ D listed in Table 2.

TABLE 3. *Molar Kerr constants at infinite dilution in carbon tetrachloride at 25°, and principal polarisabilities derived therefrom.*

Borate	$_\infty(_{\mathrm{m}}K_2) \times 10^{12}$	$(\theta_1 + \theta_2) \times 10^{35}$	$10^{23}b_1$*	$10^{23}b_2$ * = b_3 *	$10^{23}b_1$ †	$10^{23}b_2$ † = b_3 †
Trimethyl ...	$1{\cdot}2_2$	0·2902	0·919	0·903	0·993	0·866
Triethyl	$1{\cdot}7_8$	0·4233	1·398	1·370	1·489	1·324
Tri-n-propyl	$2{\cdot}5_5$	0·6065	2·011	1·973	2·124	1·916
Tri-isopropyl	$2{\cdot}5_4$	0·6041	1·996	1·965	2·111	1·908
Tri-n-butyl ...	$3{\cdot}1_7$	0·7539	2·529	2·482	2·655	2·419
Tri-isobutyl...	$3{\cdot}1_5$	0·7492	2·516	2·469	2·639	2·407
Tri-s-butyl ...	$3{\cdot}1_6$	0·7515	2·528	2·489	2·659	2·423
Tri-n-pentyl	$3{\cdot}8_4$	0·9133	3·057	3·009	3·199	2·938
Tri-isopentyl	$3{\cdot}8_4$	0·9133	3·054	3·003	3·194	2·933
Trihexyl	$4{\cdot}3_7$	1·0393	3·621	3·569	3·774	3·493
Trioctyl	$5{\cdot}6_7$	1·3485	4·599	4·546	4·778	4·457
Trinonyl	$6{\cdot}2_8$	1·4936	5·276	5·212	5·462	5·121

* Calc. on assumption that resultant moments are as in Table 2; $_{\mathrm{D}}P/_{\mathrm{E}}P$ taken as 1·1, $_{\mathrm{E}}P$ as $0{\cdot}95R_{\mathrm{D}}$.
† Calc. on assumption that $\mu_{\text{resultant}} = 0$, in which case $_{\mathrm{D}}P = {}_\infty P_2$.

Because of the allocation [11] of C_{3h} symmetry to trimethyl borate, only forms of comparable symmetry have been fully investigated. Others can be eliminated on dipole moment grounds, or by their $_{\mathrm{m}}K$'s; *e.g.*, a structure in which one OMe link is above and two OMe links are below the BO_3 plane to the maximum extents would have a μ of the order found but its $_{\mathrm{m}}K$ calc. would be $10{\cdot}8 \times 10^{-12}$, which is excessive.

A further point of interest from Table 3 is that, among the homologous normal esters, the differences per $3CH_2$ in b_1 and in $b_2 = b_3$ from one member to the next higher are roughly the same, lying about the mean value $0{\cdot}54_2 \times 10^{-23}$; this is close to the increment of polarisability to be expected ($0{\cdot}53_7 \times 10^{-23}$ c.c.) if, in passing from one homologue to the next, the new C–C links are always added in such a way that their longitudinal polarisability semi-axes make approximately semi-tetrahedral angles with the principal polarisability directions in the molecule of the lower homologue.

The authors acknowledge with gratitude a gift of specimens of trialkyl borates from Borax Consolidated Limited, of London, obtained by the kind offices of Messrs. Swift and Company Limited, of Sydney.

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[13] Barclay and Le Fèvre, *J.*, 1952, 1643.